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the size of the drop is partially recovered. There is a stage of dilution when the specific gravity is 1.0680, where the drop-size is a minimum. Further, it is seen from column 5 that the quantity of nitre in a drop increases continually as the strength of the solution increases, although both the weight and the volume of the drop vary.

Inversely, the regularity of the variation of drop-size, in the case of nitre, points to the absence of hydrates of that body.

It would be delusive to endeavour to construct a formula connecting the specific gravity with the drop-size or drop-weight of the solution; but, as before, a graphic representation serves to show the connexion between the variables. In curve D, fig. 2, the abscissæ represent the quantity of nitrate of potash in solution, the ordinates show the corresponding drop-sizes. As with chloride of calcium, it is seen that the drop-size of water is larger than that of any solution of nitre. Curve E, fig. 2, having the same abscissæ as D, has ordinates which represent the drop-weights.

It is confessedly a matter of great interest, and still greater difficulty, to determine exactly the relation which exists between a dissolved solid and its solvent—that is, to find out whether or when a solid should be viewed as being in combination with a portion of the liquid in which it is dissolved. Such questions may perhaps receive additional light from experiments similar to the above, but more extensive, and performed with this special object in view. Comparing the curves C and D, for instance, there can be little doubt that the secondary maxima and minima of C are owing to the existence of hydrates of chloride of calcium in solution. The only known hydrates of chloride of calcium are  $\text{Ca Cl}, 2\text{HO}$  and  $\text{Ca Cl}, 6\text{HO}$ , the latter of which contains 50.7 per cent. of  $\text{Ca Cl}$ . Solution S contains about 42.5 per cent. It is noteworthy that, while the six-water chloride in the solid state absorbs heat on solution, the solution S evolves heat on dilution, as already mentioned. In the case of nitre we have in the drop-sizes evidence only of the opposite efforts of two cohesions, that of the water and that of the nitre. By pursuing this direction of experimental inquiry, evidence may probably be got concerning the truth of Berthollet's hypothesis of reciprocal recomposition in the case of the mixture of the solutions of two salts,  $\text{AX}$  and  $\text{BY}$ , where  $\text{AY}$  and  $\text{BX}$  are also soluble in water.

III. "On Drops."—Part II. By FREDERICK GUTHRIE, Esq., Professor of Chemistry and Physics at the Royal College, Mauritius. Communicated by Professor STOKES, Sec.R.S. Received October 17, 1864.

We have next to consider the influence which variation in the chemical nature of the drop-forming liquid may exercise upon the drop-size in the case SLG.

The liquids which were selected for this purpose were chosen as being

typical of extensive classes, rather than as being connected with one another in immediate chemical relation. They were—

Water.	Oil of turpentine (turpento).
Alcohol.	Benzol.
Acetic acid.	Glycerine.
Acetic ether.	Mercury.
Butyric acid.	

These several liquids were allowed to drop under the same conditions, from the bottom of a hemispherical platinum cup. The arrangement of the apparatus was quite similar to that described in Part I., the ivory ball being replaced by the platinum cup, and the overflow of the cup being determined by strips of paper bent over its edge. The case of mercury is the only one which requires some explanation. A few years ago I noticed the fact that mercury which holds even a very little sodium in solution has the power of "wetting" platinum in a very remarkable manner. The appearance of the platinum is quite similar to that presented by amalgamable metals in contact with mercury. But the platinum is in no wise attacked. Further, the amalgam may be washed off by clean mercury, and the latter will also continue to adhere equally closely to the platinum. All the phenomena of capillarity are presented between the two. The surface of the mercury in a platinum cup so prepared is quite concave; and a basin of mercury may be emptied if a few strips of similarly prepared platinum foil be laid over its edge—just as a basin of water may be emptied by strips of paper or cloth, and under the same condition, namely that the external limb of such capillary siphon be longer than the internal one.

I generally use this curious property of sodium-amalgam for cleaning platinum vessels. It enables us now to examine the size of drops of mercury under conditions similar to those which obtain in the case of other liquids\*. After the cup had been used for the other liquids, its surface

\* In regard to the above-mentioned property of sodium, the following observations may be of interest. At first the explanation naturally suggests itself, that the effect wrought by the sodium may be due to an absorption of oxygen, in consequence of the oxidation of the sodium, the consequent diminution of the gaseous film between the two metals, and the resulting excess in the superior pressure of the air. This, however, cannot be the true explanation, because it is found that the perfect contact between the two, or "wetting," takes place equally well in an atmosphere of nitrogen, carbonic acid, or *in vacuo*. Hence, if I may venture upon a guess, unsupported by experimental evidence, I should be rather disposed to assign the phenomenon to the reducing action of nascent hydrogen derived from the contact of sodium with traces of water. Perhaps even the least oxidizable metals are covered with a thin film of oxide, which is reduced by the nascent hydrogen at the same moment that the mercury is presented to the reduced metal. It is found that iron, copper, bismuth, and antimony are also wetted by mercury if their surfaces are first touched with sodium amalgam. Not only do the latter metals lose this power on being heated (as we might expect, in consequence of their superficial oxidation), but platinum, from which the adhering mercury film has been wiped by the cleanest cloth, or from which it has been driven by heat, also loses the power. It is true that the surface of clean platinum is supposed to condense a

was rubbed with sodium-amalgam and washed with clean mercury. A few strips of similarly prepared platinum foil being bent over the edge and pressed close to the sides of the cup, the mercury could be handled similarly to the other liquids.

The following Table VII. shows,—

- 1. The liquids examined.
- 2. The number of drops which were weighed.
- 3. The weights found.
- 4. The mean weights of single drops.
- 5. The observed specific gravity at the given temperature.
- 6. The relative sizes of single drops.

TABLE VII.

T=26° C.

gt=2".

Radius of curvature of platinum cup=11·4 millims.

1. Name and formula of liquid.	2. Number of drops.	3. Weight of drops.	4. Mean weight of single drop.	5. Specific gravity.	6. Relative size of single drop.
		gm.	gm.		
Water..... HO.	{ 20	2·9703	0·14828	1·0000	0·14828
	{ 20	2·9923			
	{ 20	2·9472			
	{ 20	2·9603			
	{ 20	2·9533			
Glycerine ..... C <sub>6</sub> H <sub>8</sub> O <sub>6</sub> .	{ 20	2·5496	0·12804	1·2452	0·10280
	{ 20	2·5576			
	{ 10	1·2877			
Butyric acid ..... C <sub>8</sub> H <sub>8</sub> O <sub>4</sub> .	{ 20	1·1616	0·05813	1·0017	0·05803
	{ 20	1·1630			
	{ 20	1·1634			
Mercury ..... H <sub>g</sub> .	{ 20	7·9655	0·78703	13·5728	0·05798
	{ 20	7·8984			
	{ 20	7·7977			
	{ 20	7·8197			
	{ 20	0·9514			
Benzol ..... C <sub>12</sub> H <sub>6</sub> .	{ 20	0·9488	0·04778	0·8645	0·05527
	{ 20	0·9579			
	{ 20	0·9644			
	{ 20	0·8675			
Turpental ..... C <sub>12</sub> H <sub>16</sub> .	{ 20	0·8656	0·04331	0·8634	0·05016
	{ 20	0·8653			
	{ 20	0·7890			
Alcohol ..... C <sub>4</sub> H <sub>6</sub> O <sub>2</sub> .	{ 20	0·7910	0·03949	0·8163	0·04960
	{ 20	0·7896			
	{ 20	0·8214			
Acetic ether ..... C <sub>4</sub> H <sub>5</sub> O, C <sub>4</sub> H <sub>3</sub> O <sub>3</sub> .	{ 20	0·8300	0·04149	0·8930	0·04647
	{ 20	0·8384			
	{ 30	1·3636			
Acetic acid ..... HO C <sub>4</sub> H <sub>3</sub> O <sub>3</sub> .	{ 20	0·9055	0·04540	1·0552	0·04302
	{ 20	0·9095			

film of oxygen ; and the removal of this might alter the adhesion between the mercury and platinum ; but such a film could scarcely exist *in vacuo* or in another gas.

The experimental numbers obtained are given without omission. The liquids are arranged in the order of magnitude of their drop-sizes. It appears from column 5 (of the specific gravities) that some of the liquids employed were not perfectly pure. This, however, is quite immaterial in the present direction of examination, provided that in all cases where the liquids named are in future employed and compared with those of Table VII., identically the same liquids are meant.

The numbers of column 6, with which we are now exclusively concerned, present several points of great interest. In the first place, it appears that the specific gravity of a liquid is not by any means the most powerful determinant of the drop-size. Thus butyric acid, which has sensibly the same specific gravity as water, gives rise to a drop less than half the size of the water-drop; while mercury, of singular specific gravity, has no exceptional drop-size. Lastly, it may be observed how that remarkable body water asserts here again its preeminence. The first impression which these numbers make is, that there are three groups of magnitude,  $n$ ,  $2n$ ,  $3n$ . But it is possible that a change in the nature of the solid might throw these drop-sizes into a different order of magnitude; and certainly until a very much greater number of bodies is examined in this sense, it would be premature to attempt to establish anything like a law.

It is sufficient for the present to point out that the drop-size is not directly dependent upon either the specific gravity or boiling-point; nor does it stand in any obvious relation to what is sometimes called the liquidity, mobility, or thinness of a liquid. For we find that glycerine and (from former experiments) cocoa-nut oil both form smaller drops than water, the one being heavier and the other lighter than that body, and both being viscid or sluggish. On the other hand, alcohol and acetic acid, both perfectly mobile liquids, give rise to drops about half as large as those of glycerine\*.

Hence it is clear that we are still ignorant of that property of a liquid upon which its drop-size mainly depends. We are not yet in a position to connect the drop-size with any of the known physical or chemical properties of liquids. We approach the solution of the problem by studying the effects of change in some others of the variables.

The adhesion between the liquid which drops and the solid from which it drops is also affected by the curvature and general geometric distribution of the solid at and about its lowest point. And the variation in the adhesion between the solid and liquid, caused by the variation in the geometric distribution of the solid, may and does in its turn affect the size of the drop.

From this aspect, one of the simplest kinds of variation is that offered

\* The evaporation of the more volatile of these liquids is a source of slight error; not so much on account of the direct loss in weight of the drop in falling, as by reason of the cooling which it causes, and the consequent variation in density and adhesion. Such source of variation we shall examine in the sequel, and find insignificant.

by a system of spheres of various radii, but made of the same material. And this case is an important one, because it undoubtedly offers the key to all drop-size variation arising from a similar cause. To study this point we may make use of any one convenient liquid, such as water, and cause it to drop at a fixed rate from spheres of various radii, including the extreme case of a horizontal plane. This extreme case, however, presents certain practical difficulties. From a plane it is almost impossible to get a series of drops uniform in growth-time and in position. A ripe drop hanging from a horizontal plane will seek the edge thereof. Several drops may form upon and fall from the same plate at the same time and independently of one another. It is only by employing a plate not absolutely flat, that an approximation to the required conditions can be made. Taking  $r$  for the radius of curvature, the first numbers for  $r = \infty$  can therefore be considered only as an approximation. The arrangements for the other cases were quite similar to that described in Part I., fig. 3.

No. 1. A glass plate, fastened to and held by a vertical rod.

Nos. 2, 3, 4. Selected globular glass flasks.

Nos. 5, 6, &c. Perfectly spherical glass spheres.

TABLE VIII.—*Water.*

$gt = 2''$ .

$T = 22^{\circ}.5$  C.

1.	2. Number of drops.	3. Radius of curvature.	4. Weight of drops.	5. Mean weight and relative size of single drop.
1.	{ 20 }	$\infty$	gm. { 5.3325 }	0.26549
2.	{ 20 }	mm. 113.1	{ 5.2873 }	0.24808
3.	{ 20 }	70.1	{ 4.9226 }	0.22619
4.	{ 20 }	47.2	{ 5.0007 }	0.21257
5.	{ 20 }	17.5	{ 4.5260 }	0.17497
6.	{ 20 }	15.1	{ 4.5218 }	0.16765
7.	{ 20 }	11.5	{ 4.2781 }	0.15122
8.	{ 20 }	11.2	{ 4.2249 }	0.14896
9.	{ 20 }	10.0	{ 3.5055 }	0.14321
10.	{ 20 }	7.5	{ 3.4733 }	0.13356
11.	{ 20 }	7.1	{ 3.3562 }	0.12877
	{ 9 }		{ 3.3500 }	
			{ 3.0281 }	
			{ 3.0206 }	
			{ 2.9803 }	
			{ 2.9780 }	
			{ 2.8665 }	
			{ 2.8619 }	
			{ 2.6765 }	
			{ 2.6660 }	
			{ 2.5752 }	
			{ 1.1591 }	

It appears, therefore, that the drop increases in size according as the radius

of the sphere increases from which the drop falls, and, further, that the difference of drop-size brought about by this cause alone may easily amount to half the largest drop-size. For dispensers of medicine this fact is as important as that pointed out in Part I., where it was shown that the growth-time so materially influenced the drop-size. The lip of a bottle from which a drop falls is usually annuloid. The amount of solid in contact with the dropping liquid is determined by the size of two diameters, one measuring the width of the rim of the neck, the other the thickness of that rim. In most cases the curvature and massing of the solid at the point whence the liquid drops is so irregular as not to admit of any mathematical expression.

The reason why drops which fall from surfaces of greater curvature are larger than those which fall from surfaces of less curvature is surely this:—In the case of a surface of greater curvature the base of the drop has more nearly its maximum size; the centre of gravity of the liquid film from which the drop hangs is nearer to the centre of gravity of the hanging drop; the contact between the two is more extensive and intimate; so that the drop is held for a longer time and therefore grows more.

On comparing columns 3 and 5 of Table VIII., there does not appear to be any obvious law of connexion between the two; nor indeed can the numbers of column 4 pretend to such a degree of accuracy as would justify us in attempting to establish one. This is seen on comparing *inter se* the numbers of column 4. Especially with the spheres of longer radii, there is so much difficulty in getting a uniform wetting of the surface whence the drop falls, and this so materially influences the drop-size, that the numbers found are seen to vary considerably. Greater accord is obtained with spheres of less radii. As we might expect, the same absolute increase in length of radius takes less effect upon the drop-size in the case of longer than in that of shorter radii. The infinite, or at least indefinitely great difference between the radii 1 and 2 produces about the same effect upon the drop-size as the difference of 43 millims. between the radii 2 and 3, and so on.

The following Table of first differences shows this more strikingly:—

$r_{n+1} - r_n$	$w_{n+1} - w_n$
$\infty$	0.01854
43	0.02189
22.9	0.01362
29.7	0.03760
2.4	0.00732
3.6	0.01643
0.3	0.00226
1.2	0.00575
2.5	0.00965
0.4	0.00479

The relation exhibited in this Table supports the supposition that the size of the drop varies inversely as the contents of a figure bounded below by a circular horizontal plane of constant diameter (less than that of the

sphere) tangent to the sphere, laterally by a cylinder of vertical axis standing on the tangent plane and cutting the sphere, and above by the convex surface of the sphere itself (Plate IV. fig. 4).

As the diameter of the sphere still further diminishes, the size of the drop is limited by the possible size of its base, until finally the sphere is completely included in the drop.

It would be interesting, but it would take us too far, to consider the various cases of liquids dropping from cones, edges, solid angles, cylinders, rings, &c. We must content ourselves in this direction with the fact that the size of a drop is greater the more nearly plane is the surface from which the dropping takes place. If it were possible for a drop to fall from a concave surface, we should anticipate a still further increase in its size.

The relation between drop-size and curvature may be more strikingly shown by arranging the spheres one above the other in the order of magnitude.

Plate IV. fig. 5.—Each sphere receives the drops from the higher one. The quantity of water which drops in a given time, from every sphere, is the same. Hence in all cases the number of drops is inversely as the drop-

TABLE IX.—*Water.*

$$gt = 2''.$$

$$T = 23^{\circ} \text{ C.}$$

1. Radius of disk.	2. Number of drops.	3. Weight of drops.	4. Mean weight and relative size of single drop.
in.		grm.	
$\frac{5}{20}$	$\left\{ \begin{array}{l} 20 \\ 20 \\ 20 \\ 20 \\ 20 \end{array} \right.$	$\left\{ \begin{array}{l} 3.3682 \\ 3.1193 \\ 3.2523 \\ 3.3256 \\ 3.2594 \end{array} \right.$	0.16325
$\frac{4}{20}$	$\left\{ \begin{array}{l} 20 \\ 20 \\ 20 \\ 20 \end{array} \right.$	$\left\{ \begin{array}{l} 2.9693 \\ 2.9854 \\ 2.9746 \\ 3.0031 \end{array} \right.$	0.14915
$\frac{3}{20}$	$\left\{ \begin{array}{l} 20 \\ 20 \\ 20 \\ 20 \end{array} \right.$	$\left\{ \begin{array}{l} 1.9333 \\ 1.9244 \\ 1.9504 \\ 1.9248 \end{array} \right.$	0.09666
$\frac{2}{20}$	$\left\{ \begin{array}{l} 20 \\ 20 \\ 20 \\ 20 \end{array} \right.$	$\left\{ \begin{array}{l} 1.4618 \\ 1.4672 \\ 1.4688 \\ 1.4682 \end{array} \right.$	0.07332
$\frac{1}{20}$	$\left\{ \begin{array}{l} 20 \\ 20 \\ 20 \end{array} \right.$	$\left\{ \begin{array}{l} 0.8250 \\ 0.8212 \\ 0.8208 \end{array} \right.$	0.04107
	$\left\{ \begin{array}{l} 20 \end{array} \right.$	$\left\{ \begin{array}{l} 0.8190 \end{array} \right.$	

size; so that by counting the number of drops which fall from any two spheres in the same time, we get at once the relative sizes of the respective



drops. For several reasons, this plan of comparison is not sufficiently accurate to measure drop-sizes; but it offers a method of making the difference of drop-size visible to any number of persons at once.

The only other variation in the geometrical relation between the solid and the liquid, which we shall consider, is the variation in the size of a circular horizontal plane from which drops fall.

Five disks of copper foil were cut of the radii  $\frac{5}{20}$ ,  $\frac{4}{20}$ ,  $\frac{3}{20}$ ,  $\frac{2}{20}$ ,  $\frac{1}{20}$ th of an inch respectively. These were fastened horizontally to vertical wires, and, having been thoroughly cleaned by momentary immersion in nitric acid and washing, water was made to drop from them at the rate  $gt=2''$ .

Table IX. shows the influence of this kind of variation upon drop-size. The want of accord in the numbers of the largest disk is owing to a peculiar tremor which the drops exhibit at the moment of delivery. The same phenomenon was noticed, but to a less extent, with the next smaller disk. With the remainder it was not noticed.

The curvature and shape of the solid, and its consequent massing towards the liquid, is intimately connected with the next phase of variation which we shall consider, to wit, the variation in the chemical composition of the solid from which the drop falls. The influence of this kind of variation is to be studied by examining the size of drops formed under like circumstances, from spheres of the same size, but made of different material. Since in this case the liquid remains the same, we must limit the solids examined to such as the liquid completely wets. In this case, variation in the drop-size implies a variation in the thickness of the liquid film covering the solid. The latter must be caused by variation in the adhesion between the solid and liquid. Finally, such adhesion can only vary through one or both of two causes—namely, variation in the density of the solid, or in its specific adhesion dependent upon its chemical nature.

The first qualitative experiment was made upon three equal spheres of brass, glass, and cork. They were hung one above the other in the manner before described, so that the drop from one sphere fell upon the lower one\*. It was found that, in whatever order the spheres were arranged, when the flow was uniform and not quicker than  $gt=2''$ , the dropping from the cork took place with the greatest rapidity, that from the glass next, and that from the brass most slowly—showing that the brass gives rise to the largest, the glass to the next largest, and the cork to the least drops. From this it would seem that the drops are in the same order as to size as are the solids as to density. We shall find, however, that this is not always the case, and that some other property as well as density is at work to influence the drop-size. The quantitative experiment, the results of which are given in Table X., confirms the result of the qualitative experiment given above, but shows, at the same time, that the joint influences of den-

\* In this kind of experiment there should be a considerable mass of cotton wool on each sphere to receive the drops from the higher one, and, by acting as a reservoir, to regulate the flow.

sity and chemical diversity of the solid have only a small effect upon the drop-size. The conditions of the experiment were similar to those previously described.

TABLE X.—*Water.*

$$gt=2''.$$

$$T=22^{\circ}.9\text{ C.}$$

$$r=7.1\text{ millims.}$$

$$\text{Number of drops}=20.$$

Substance.	Weight of 20 drops.	Mean weight of single drop.
	grms.	gm.
Cork .....	$\left\{ \begin{array}{l} 2.4846 \\ 2.4848 \\ 2.4832 \\ 2.4789 \\ 2.4821 \\ 2.4877 \end{array} \right\}$	0.12418
Glass .....	$\left\{ \begin{array}{l} 2.5930 \\ 2.5985 \\ 2.5989 \\ 2.5949 \\ 2.5953 \\ 2.5900 \end{array} \right\}$	0.12975
Brass .....	$\left\{ \begin{array}{l} 2.6225 \\ 2.6229 \\ 2.6260 \\ 2.6295 \\ 2.6296 \\ 2.6116 \end{array} \right\}$	0.13118

When a liquid drops from a solid it is not always that the adhesion between the solid and liquid is overcome. The phenomenon of "wetting" implies a superiority of the adhesion between the solid and liquid over the cohesion of the liquid; and in all cases where a liquid drops from a solid which it wets, the act of separation is a disruption of the liquid, and not a separation of the liquid from the solid; that is, the separation of the drop is a failure of cohesion and not of adhesion. We are not, however, justified on this account in anticipating that the size of a drop is unaffected by the chemical nature of the solid from which it drops, even in those cases where the adhesion between the solid and liquid is greater than the cohesion of the liquid (that is, where the liquid completely wets the solid), because, although it is the liquid which is broken, yet the size of the broken-off part, or drop, depends in great measure upon the thickness of the residual film, as we have seen in examining the influence of the growth-time (in Part I.) and of the radius of curvature.

Adhesion may also exist between a solid and a liquid which does not wet it, as when a drop of mercury hangs from a glass sphere. But the cohesion of the liquid in such a case, by its effort to bring the liquid to the spherical form, and the weight of the drop so modify the adhesion between

the solid and liquid, by altering the size of the surface of contact between the two, that the size of the drop gives no direct clue to the cohesion of the liquid.

We may now examine a few cases in which, the size of the sphere remaining the same, and its density in some instances nearly so, the matter of the solid varies, but the liquid wets it in all cases. This will show whether the differences of Table X. are due wholly to differences of density of the solid, or also or wholly to differences of chemical constitution.

TABLE XI.—*Water.* $gt=2.$  $T=23^{\circ}\text{C}.$ 

Radius of curvature=7 millims.

1. Substance.	2. Weight of 20 drops.	3. Mean weight of single drop.	4. Specific gravity of solid.
	grms.	gm.	
Antimony .....	$\left. \begin{array}{l} 2.3905 \\ 2.3980 \\ 2.3968 \\ 2.4016 \end{array} \right\}$	0.11984	6.80
Sulphur .....	$\left. \begin{array}{l} 2.4019 \\ 2.4067 \\ 2.4046 \\ 2.4063 \\ 2.4022 \end{array} \right\}$	0.12021	2.00
Cadmium .....	$\left. \begin{array}{l} 2.4362 \\ 2.4387 \\ 2.4374 \\ 2.4358 \end{array} \right\}$	0.12185	8.70
Zinc .....	$\left. \begin{array}{l} 2.4495 \\ 2.4481 \\ 2.4518 \\ 2.4478 \end{array} \right\}$	0.12246	6.86
Lead .....	$\left. \begin{array}{l} 2.4522 \\ 2.4525 \\ 2.4537 \\ 2.4528 \end{array} \right\}$	0.12264	11.44
Phosphorus ...	$\left. \begin{array}{l} 2.4532 \\ 2.4564 \\ 2.4528 \end{array} \right\}$	0.12274	2.08
Bismuth .....	$\left. \begin{array}{l} 2.4584 \\ 2.4580 \\ 2.4589 \end{array} \right\}$	0.12285	9.90
Tin .....	$\left. \begin{array}{l} 2.4843 \\ 2.4864 \\ 2.4829 \\ 2.4861 \end{array} \right\}$	0.12425	7.29

Equal spheres of the substances were made by casting them in the same bullet-mould. The surfaces of the metals were roughened by momentary immersion in acid; tin and antimony in hydrochloric, the rest in nitric acid. Without this precaution a metallic surface is apt to be wetted only locally, the base edge of the drop is irregular and inconstant, and the drop-

weight varies. Indeed with some metals, such as tin, a smooth and bright surface is scarcely wetted by water.

As the bodies examined have different coefficients of expansion by heat, and one of them expands on solidification, it was necessary to test the equality of their size and remedy any inequality. This was done by arranging three of them, one at each angle of a small equilateral triangle drawn on a large piece of plate glass. Another piece of plate glass was then placed upon the spheres so as to rest on them all three, and slightly loaded. On passing a gauge between the plates, at their edges, the slightest inequality of the spheres could be detected, because the gauge lifted the plate off the smallest of the three balls, which could then be moved. The larger spheres were then reduced in size by brisk agitation in acid. The sulphur and phosphorus were, for the same purpose, washed in ether.

Although there is only a slight difference between the consecutive terms of column 3, yet between the extremes of antimony and tin a well-marked difference exists.

This Table shows that the drop-size stands in no simple relation either to the equivalent density or chemical character of the solid, and establishes the existence of a specific adhesion independent of these. Although the differences of Table IX. may be partly owing to the differences of density of the solids cork, glass, and brass, yet we see from Table X. that there is about half as great a difference between the sizes of drops from antimony and tin as between those from cork and brass, although the difference of density between the first two is small compared with that between the last. Again, sulphur gives rise to drops intermediate between those of antimony and cadmium. Without, therefore, venturing to assert that density is without influence on drop-size, it is clearly proved that it does not exert the most powerful influence.

We have finally to examine the direction and extent of variation in drop-size caused by change of temperature. By altering the density of the liquid, a change in its temperature may affect the drop-weight without altering the drop-size. It may further alter the drop-size by altering the size and therefore the curvature of the solid. Any error introduced by the first of these sources is eliminated by dividing the observed weight by the specific gravity at the proper temperature, as in the case of different liquids at the same temperature. Errors from the second source may be certainly safely neglected, being far within the errors of observation.

In the place where these experiments were made, the range of natural atmospheric temperature is very small. From the coldest to the hottest season the difference scarcely exceeds  $10^{\circ}\text{C}$ . This circumstance made an extended and minute study of the influence of temperature impossible, by preventing more than one observation at each temperature being made.

The liquid taken was water, and the solid was glass. The water was heated to the boiling-point and placed in the apparatus (Part I. fig. 3). The sphere from which the water fell was the bulb of the thermometer which

measured the temperature. Fully the upper half of the sphere was covered with cotton-wool, so that the whole of the sphere was kept wet. The considerable mass of mercury in the bulb of the dropping sphere or thermometer itself served to make more uniform the temperature of the drops ; while the actual contact between the drops and the spherical bulb ensured a tolerably close approximation between the actual temperature of the drops and that indicated on the stem of the instrument. Although, therefore, the temperatures observed cannot pretend to any even approximate positive accuracy, yet they are certainly in the actual order of magnitude. The arrangement is seen in Plate IV. fig. 6.

TABLE XII.—*Water.*  
 $gt=2''$ .  
 $r=7\cdot4$  millims.  
Number of drops=20.

Temperature, Centigrade.	Weight of 20 drops.	Weight of single drop.	Relative mean size of single drop (corrected for temperature).
	grms.	grm.	
40·3 {	44·1	2·5564	0·12782
	40·	2·5795	
	37·	2·5826	
	35·	2·6083	
	33·9	2·6105	
	32·6	2·6161	
30·6 {	31·2	2·5960	0·12980
	30·6	2·6065	
	29·	2·6044	
	28·2	2·5983	
	28·	2·6078	
	27·5	2·6032	
20·4	20·4	2·6480	0·13240

In the above Table the temperatures are so grouped together that the means of the groups differ from one another by about 10° C. The single drop-weights are correspondingly grouped, and the mean of each group is then divided by the specific gravity of water (0°=1) at the mean temperature of the group.

It appears then that, for a range of 20° Centigrade, or 36° F., the difference in drop-size effected by change of temperature in the liquid is inappreciably small, not being more than 0·00277, a quantity almost within the limits of experimental error ; for on referring to Table X. we find that the greatest difference between the numbers for glass, which should be equal, amounts to 0·00044 grm., or a sixth of the greatest difference due to variation in temperature.

On the whole, then, we may conclude that the temperature has very little influence on the drop-size in the case of water between the above limits. No doubt, near the point of solidification, where liquids have an incipient

structure, the drop-size would be subject to sudden changes of magnitude. A few experiments with other liquids, namely turpentine, acetic acid, and alcohol, showed that with them the drop-size was almost equally insensible to change of temperature; and in all cases, as with water, the lower the temperature, on the whole, the larger the drop.

We have now examined *seriatim* all the chief causes upon which the drop-size depends in the case SLG. They are, 1. Rate of delivery; 2. Solids held in solution; 3. Chemical nature of liquid; 4. Geometric relation between solid and liquid; 5. Density and chemical nature of solid; 6. Temperature.

Our data, however, are still insufficient for us to predict, under all circumstances, the relative sizes of the drops of liquids under known external conditions. Clearly the missing term is closely related to the specific cohesion of the liquid. But what is cohesion? and how can it be measured? It lies perhaps in the nature of things—it seems at least inevitable—that the nomenclature of elementary properties should be vague and unsatisfactory. The properties of solids—hard, soft, brittle, tough, tenacious, elastic, malleable—do not stand in any definite relation to one another. Even the hardness which resists abrasion, the hardness which resists penetration, the hardness which resists crushing are by no means identical; so that one body may possess more of the one sort of hardness than a second body does, while the second body exceeds the first in another sort of hardness. Nor do any of the above-mentioned properties of solids stand in any simple relation to that resistance to the separation of the contiguous parts which is called cohesion. Thus, by no attribution of this single property of cohesion could we define ice or shell-lac, bodies which are at the same time tough, brittle, elastic, and soft.

We are forced to the conception of two distinct kinds of cohesion—*stubborn* and *persistent*. These may coexist, but are not identical. The one is strong to assert, the other pertinacious to maintain. The four following substances may serve to illustrate the possession of these two cohesions in various quantity.

Talc has little stubborn and little persistent cohesion.

Glass has much stubborn and little persistent cohesion.

Gold has little stubborn and much persistent cohesion.

Iron has much stubborn and much persistent cohesion.

The necessity for such a discrimination exists in a yet higher degree in liquids. If we conceive two liquids of different nature dropping from the same substance which they both wet, and if there be only one kind of cohesion, the one which has the greatest cohesion will tend most strongly to assume the spherical form; and this would tend to cause it to drop sooner, or have a smaller drop-size than the other. On the other hand, the liquid of stronger cohesion will cling most strongly to the film of liquid adhering to the solid; this will keep it longer from falling, and thereby increase its drop-size. Hence an increase of cohesion tends to produce two contrary

effects. But if there be a similar distinction between the two kinds of cohesion of liquids, as above pointed out in the case of solids, we have the following consequence. It is the persistent cohesion which causes the assumption of the spherical form, the stubborn which resists the separation of the drop. The former tends to diminish, the latter to increase its size. As one or other predominates, the size of the drop varies.

Accordingly the drop-size is by no means a measure of what is generally called the cohesion of the liquid, but rather a measure of the difference between the two cohesions, stubborn and persistent; and the law is, that the drop-size varies inversely as the persistent, and directly as the stubborn cohesion of the liquid.

In mercury, water, and glycerine the stubborn cohesion is greater in proportion to the persistent cohesion than in the other liquids examined; but it by no means follows that persistent cohesion is wanting in mercury or stubborn in alcohol.

When a drop is in the act of falling its stubborn cohesion is in equilibrium with the resultant of two forces—the one, the persistent cohesion, tending to produce a spherical form, the other the weight of the drop. Since the former of these component forces is, for the same liquid, constant, it seems as though the weight of the drop might be taken as a measure and expression of the stubborn cohesion. But such is not the case, because we have no ground for supposing that the diameter of the drop where the separation occurs is of constant size; on the contrary, it must be conceded that in larger drops this hypothetical surface of stubborn cohesion is larger than in smaller drops. Further, unless we know the exact shape of a drop in all cases, we are not in a position to deduce the size of the surface of cohesion from the drop-size or drop-weight.

In the cases where it has been tried, it has not been found that the nature of the gaseous medium in the case of SLG exerts any appreciable or definite influence upon the drop-size. Taking glass for the solid and water for the liquid, the medium was changed from air to nitrogen, hydrogen, and carbonic acid. The exceedingly slight variation wrought in the drop-size by this change may probably have been due to the different solubility of the gases in water, and the consequent alteration in the cohesion of that liquid.

Having now traced the effect of variation in the conditions which determine the size of a drop in the general case SLG (or where from a solid a liquid drops through a gas), we come to the case SLL (that is, where from a solid a liquid drops through a liquid). As in the cases of SLG, we must here also take the three terms of such chemical nature as to be without action upon one another.

SLL. *From a Solid a Liquid drops through a Liquid.*

A preliminary quantitative experiment was made under the following conditions:—Water was made to drop from a glass sphere at the rate

$gt=5''$ . The drops were collected in a tube bearing an arbitrary mark. The number of drops required to fill the tube up to this mark was noted. Then the sphere was surrounded by turpental, and the rate having been brought again\* to  $gt=5''$ , the number of drops of water necessary to fill the tube up to the same mark was counted. The turpental being replaced by benzol, the same operation was performed. The entire arrangement of the Stalagmometer† is seen in Plate V. fig. 7.

X, Y are contrivances described in Part I. for giving a uniform flow of water.

The siphon A rests upon the cotton-wool covering half of the dropping sphere and thermometer-bulb G. The sphere is held by its stem B in the clamp H. C is half a globular 1-lb. flask, supported by the filter-stand K. Through the neck of C passes the tube D. C and D are joined liquid-tight by the caoutchouc collar L. A few arbitrary marks are made at E. The lip of C is turned down to a beak at M above the vessel F.

In adjusting the instrument, to get the required value of  $gt$ , the holder K is slipped along the table so that the drops from G fall between C and D, and not into D. When the required rate is obtained, it is slipped back again. When such liquids as turpental are used as media, a little water is poured between D and C to protect the caoutchouc. In all cases where a liquid medium is employed C is filled till it runs over.

In the first experiment, of which the results are given in the following Table XIII., the numbers are subject to two sources of error. The volume filled is rather small, and no allowance is made for meniscus. In this, as in all cases of SLL, great care must be taken not to shake the instrument.

TABLE XIII.—*Water.* $gt=5''$ . $T=22^{\circ}\text{C.}$ Radius of glass sphere= $7\cdot4$  millims.

1. Medium.	2. Number of drops of water required to fill a given volume.	3. Mean of Column 2.	4. Relative size of single drop (through air=1).
Air .....	$\begin{Bmatrix} 58 \\ 56 \end{Bmatrix}$	57·0	1·0
Turpental .....	$\begin{Bmatrix} 28 \\ 27 \\ 26 \\ 26 \end{Bmatrix}$	26·7	2·14
Benzol .....	$\begin{Bmatrix} 7 \\ 7 \end{Bmatrix}$	7·0	8·14

There is therefore a greater difference between the drop-sizes of water in benzol and turpental than between those in turpental and air. The tur-

\* A diminution of  $gt$  is observed.

† Σταλαγμὸς, a drop.



pentol and benzol here employed had the specific gravities of 0.863 and 0.864 respectively; they may therefore be considered of equal density. Hence variation in the liquid medium, independent of variation in its density, produces an enormous effect upon drop-size. We shall have occasion to return to this case.

The influence which the liquid medium exerts on the drop-size, and the share of that influence due to the specific gravity of the medium, will be well seen on comparing the drop-sizes of mercury which falls through various liquid media.

The arrangement of the apparatus for this purpose is seen in Plate V. fig. 8. As far as A it is similar to fig. 7. The siphon A, fig. 8, is a capillary tube; its lower end, which is turned vertically downwards, rests upon a sphere of brass, R, which has been washed with nitric acid and sodium-amalgam, and allowed to soak for some days under mercury. Mercury adheres perfectly to such a sphere. In every case the sphere was immersed just halfway in the liquid. A small capsule S is supported in the liquid on a stand T about half an inch lower than the bottom of the sphere. As soon as  $gt=5''$  becomes constantly  $=5''$ , the vessel V is moved so that S comes under R. Five drops of mercury having been caught, the cup is moved horizontally as before, taken out and replaced by a fresh one, and so on. The batches of five drops are washed, dried, and weighed. The results are given in Table XV.

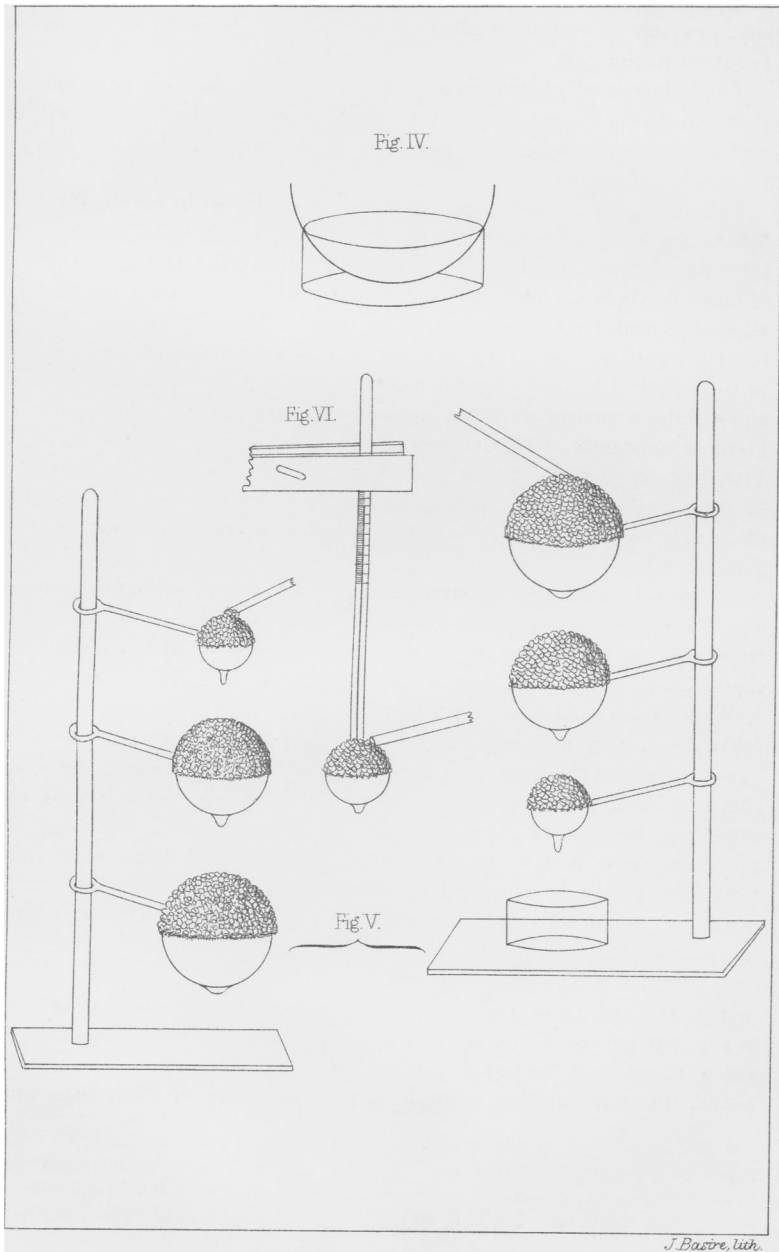
We may, however, previously notice here with advantage a phenomenon which attends the separation of drops under several circumstances, but which can be watched most narrowly in the cases of SLL, because in a liquid the separation of a drop is less abrupt than in a gas.

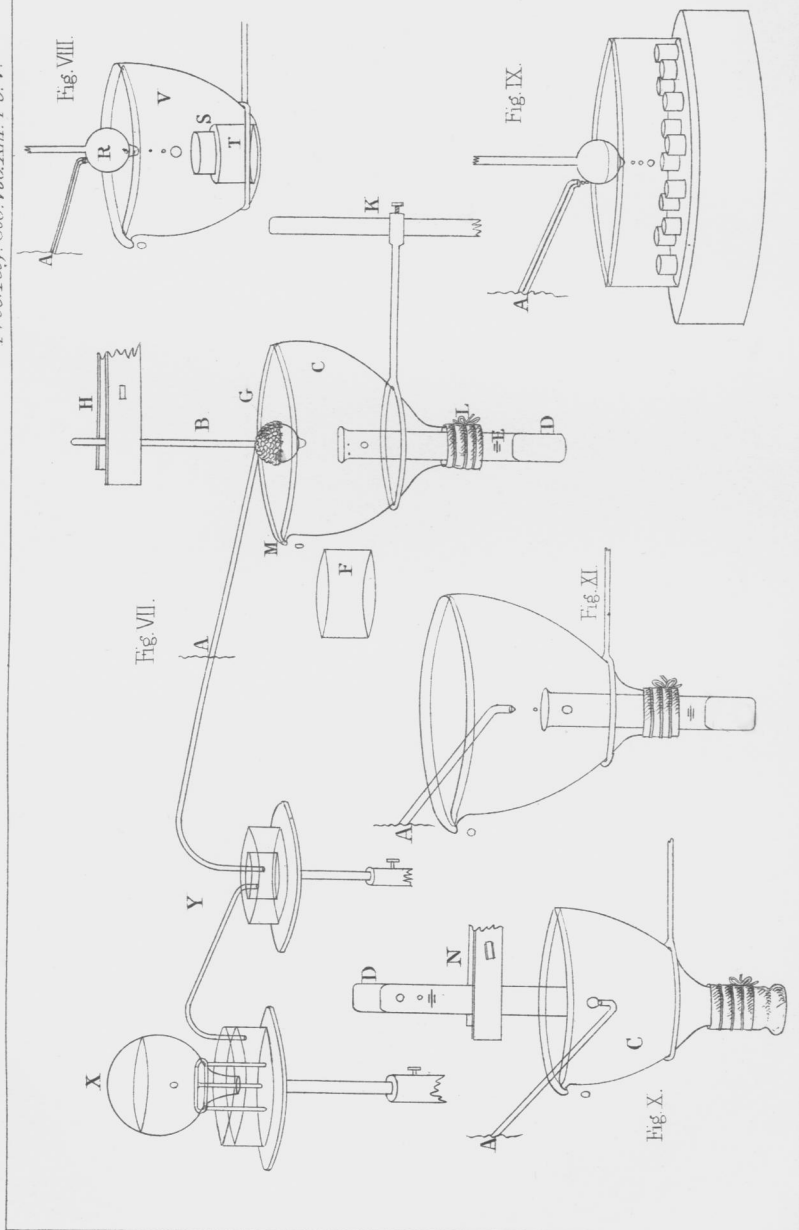
When water falls from glass through air, immediately after the drop separates, a very minute drop is frequently projected upwards from the upper surface of the drop\*. I have not traced the conditions under which this supplementary drop is formed; indeed it is sometimes formed, and sometimes not, under apparently similar circumstances. No doubt the proximate cause is that the drop at the instant of separation is not spherical; the persistent or retentive cohesion, which brings it almost immediately to its normal shape, does not allow time for its more excentric parts to collect to the main mass; they are therefore by the motion of the main drop flung off and projected upwards.

The same phenomenon is seen much more distinctly when water drops at this rate ( $gt=5''$ ) through benzol or turpental. In these cases the persistent cohesion of the liquid medium comes also into play.

But the most striking example of supplementary drops is seen when

\* The secondary drop may be well shown by holding a plate containing anhydrous cupric sulphate about two inches below the dropping solid. The white salt is smoothened by pressure under a plate, and its surface, being porous, absorbs the water-drops instantly and without splashing. The blue spots of hydrated sulphate show where the water has fallen.





glycerine forms the medium through which mercury drops. In this case, when  $gt=5''$ , there are always two supplementary drops of mercury formed. It is impossible to determine whether they both have their origin at the same moment and from the same drop. The probability, however, is that they have not, but that one is first separated from the main drop, and the second from the first; for there is always a great disparity between the sizes of the two supplementary drops, whereas, if they were both formed at the same time and for the same reason, we should be justified in expecting greater equality. The drops soon separate in falling, in consequence of the difference of their surfaces. The relative sizes of the main and supplementary drops in the case of mercury falling from copper through glycerine were determined as follows:—A number of porcelain cups (fig. 9) were arranged at the bottom of a shallow dish full of glycerine; when the rate of dropping was uniform at  $gt=4''$ , the dish was shifted horizontally so that every drop with its two supplements was caught in a separate cup. The globules of mercury in each cup were removed by a little scoop of copper foil. Ten of each kind were collected. After washing and drying, they were weighed, with the following result:—

TABLE XIV.—*Mercury.* $gt=4''$ . $T=21^{\circ}3$  C.

Radius of sphere = 12.8 millims.

	grms.
10 principal drops weighed .....	6.3447
10 first supplementary drops weighed ....	0.1242
10 second do. do. do. ....	0.0229
10 complete drops weighed .....	6.4918

In all cases of SLL the supplementary drop or drops were collected and weighed or measured with the main drop.

In Table XV.—

Column 1 shows the medium through which the mercury dropped.

Column 2. The number of drops weighed.

Column 3. The weight of the drops. The weight of every batch of drops is given, in order that the approximation between the figures for each liquid may be compared with that between the separate liquids. In two cases only, marked by an asterisk, are the numbers probably erroneous. They are not reckoned in taking the mean.

Column 4. Mean weight of single drop, from column 3.

Column 5. Specific gravity of medium.

Column 6 shows the weight of the drop of mercury *in the liquid*. Since the falling of the drop is determined in part by its weight, and since the weight depends not only upon the size of the drop, but also upon the density of the medium in which it is formed, it is interesting to see how the

size of the drop is affected by the diminution in its weight caused by the density of the medium.

If  $W_1$  = weight of drop of mercury in air,

$W_2$  = required weight of drop of mercury in liquid,

$A$  = specific gravity of liquid,

$B$  = specific gravity of mercury ;

then  $W_2 = W_1 - \frac{A}{B} W_1.$

The values of  $W_2$  form column 6.

The liquid media are arranged according to the order of magnitude of the numbers of column 4. The salient points of Table XV. are chiefly these :—

1. *The drop-size of a liquid which drops under like conditions through various media does not depend wholly upon the density of the medium and consequent variation in the weight, in the medium, of the dropping liquid.* Thus glycerine, whose density is above that of all the other liquids examined, does not, as a medium, cause the mercurial drop to assume either its minimum or maximum size.

2. The liquids in Table XV. are in the same order as in Table VII. In other words, *if there be two liquids, A and B, which drop under like conditions through air, and the drop-size of the one, A, be greater than that of the other, B ; then if a third liquid, C, be made to drop through A and through B, the drop-size of C through A is greater than the drop-size of C through B.*

3. Further, on comparing Tables XIII. and XV. it appears that, whether water or mercury drops through turpental and benzol, the drop through benzol is greater than the drop through turpental. This we shall afterwards find confirmed in other instances into the law, *If the drop-size of A through B be greater than the drop-size of A through C, then the drop-size of D through B is also greater than the drop-size of D through C.*

It is further observed that, while mercury exhibits its largest drop when falling through air, water assumes its smallest drop-size under this condition.

This method of the examination of liquids by drop-size in the case SLL, which brings so prominently forward a comparatively slight difference between similar liquids, may be used, not only to detect commercial adulterations of one liquid by another, but perhaps to distinguish between those remarkably-related isomeric liquid bodies (the number of which is quickly increasing) between whose terms the difference has until lately escaped detection. Of these bodies perhaps the first most remarkable instance was furnished by the two amylic alcohols ; but the greatest number at present known is amongst the hydrocarbons.

We may take an example illustrating the use of the stalagmometer in approximately measuring the proportion, in a mixture, of its two chemically and physically similar, but not isomeric constituents.

Suppose we had a liquid which we knew to consist wholly of a mixture of benzol and turpental, and we wished to find the proportion in which

TABLE XV.—*Mercury.* $gt = 5''$ . $T = 21^{\circ}.3 \text{ C.}$ 

Radius of sphere = 12.8 millims.

1. Medium through which the mercury dropped.	2. Number of drops.	3. Weight of drops.	4. Mean weight in air and relative size of single drop.	5. Specific gravity of medium.	6. Weight of single drop in respective medium.
Air .....	$\left( \begin{array}{c} 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \end{array} \right)$	grms. $\left\{ \begin{array}{c} 3.8123 \\ 3.8138 \\ 3.8169 \\ 3.8389 \\ 3.8141 \\ 3.8131 \\ 3.8182 \\ 3.8557 \\ 3.8430 \\ 3.8105 \\ 3.8535 \end{array} \right\}$	gm.  0.76545	0.00	0.76545
Water.....	$\left( \begin{array}{c} 5 \\ 10 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \end{array} \right)$	$\left\{ \begin{array}{c} 3.5037 \\ 6.9384 \\ 3.4534 \\ 3.5047 \\ 3.4918 \\ 3.5015 \\ 3.5066 \end{array} \right\}$	0.69750	1.00	0.64619
Glycerine .....	$\left( \begin{array}{c} 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \end{array} \right)$	$\left\{ \begin{array}{c} 3.4235 \\ 3.4215 \\ 3.4235 \\ 3.4285 \\ 3.3627* \\ 3.4088 \\ 3.4083 \\ 3.4329 \\ 3.4090 \\ 3.3981 \end{array} \right\}$	0.61508	1.245	0.55793
Benzol .....	$\left( \begin{array}{c} 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 10 \end{array} \right)$	$\left\{ \begin{array}{c} 2.9418 \\ 2.4875* \\ 3.0773 \\ 2.9888 \\ 2.9637 \\ 2.9549 \\ 3.0767 \\ 2.9583 \\ 2.9352 \\ 6.0144 \end{array} \right\}$	0.59822	0.864	0.56014
Turpental .....	$\left( \begin{array}{c} 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \\ 5 \end{array} \right)$	$\left\{ \begin{array}{c} 2.1427 \\ 2.1900 \\ 2.1883 \\ 2.1960 \\ 2.1820 \\ 2.1620 \\ 2.1768 \\ 2.1791 \\ 2.1608 \\ 2.1708 \end{array} \right\}$	0.43497	0.863	0.40715

these two ingredients were present. We could scarcely approach to an answer by any of the means hitherto employed. The specific gravities of the two liquids are so close ( $\cdot 864$ ,  $\cdot 863$ ) that the density of the mixture would give us no substantial aid. Though there is a considerable difference ( $80^{\circ}$  C.) in their boiling-points, no one who is familiar with the difficulties of fractional distillation would place any reliance upon a quantitative separation based upon volatility. Their refractive indices are nearly the same\*. Their vapour-densities,  $2\cdot 77$ ,  $4\cdot 76$ , though comparatively different, are not absolutely very wide apart. They are active and passive towards most of the same chemical reagents, and interfere with one another's reactions. If we have recourse to chemical analysis ( $C_{12}H_6$ ,  $C_{20}H_{16}$ ), a very small experimental error would point to a great difference in the proportion of the two.

To find how far the stalagmometer (Plate V. fig. 7) is applicable in this case, it was filled with five liquids in succession:—

- 1st, with benzol . . . . . = B.  
 2nd, with two volumes benzol and one of turpental =  $B_2T$ .  
 3rd, with one volume benzol and one of turpental . =  $BT$ .  
 4th, with one volume benzol and two of turpental =  $BT_2$ .  
 5th, with turpental . . . . . = T.

The time-growth being brought in each case to  $5''$ , the number of drops of water required to fill a given volume was counted, allowance being made for the meniscus.

TABLE XVI.

Through.....Air.	T.	BT <sub>2</sub> .	BT.	B <sub>2</sub> T.	B.	
102	51	38	34	31	14	
102	51	37	33	31	14	
101	50	38	33	31	14	
..	49	..	..	..	..	
Mean. . . .	101·7	50·2	37·7	33·3	31	14

Hence a difference of 16·6 per cent. in one of the constituents corresponds to an observed difference, under the most unfavourable conditions, of three drops. In other words, the stalagmometer is sensitive to an alteration of about 6 per cent. By increasing the capacity of the recipient, it is clear that the drop-numbers, and therefore their differences, might be increased at pleasure. Thus by counting the number of drops necessary to fill a volume six times the size, we could tell to within one per cent. how much turpental and how much benzol were present.

But it is perhaps in the cases of the still more proximate identity of isomeric bodies mentioned above that the stalagmometer may be used rather

\* The refractive index of turpental is  $1\cdot 476$ ; that of benzol does not appear to have been measured; but that it is almost identical with that of turpental is seen on mixing the two. In those cases in which I propose chiefly to use the stalagmometer, namely with isomeric liquids, the method of refraction is useless, because isomeric liquids seem always to have the same refractive indices.

as a stalagmoscope, to render evident rather than to measure a difference of drop-size.

From Table XVI. we gather the general law concerning three liquids, two of which are insoluble in the third. *If a liquid, A, drop downwards under like conditions in succession through two liquids, B and C, then its drop-size through any mixture of B and C is intermediate between its drop-size through B and its drop-size through C; and the greater the proportion of  $\frac{B}{C}$  in the mixture, the more nearly does the drop-size of A through the mixture approach to the drop-size of A through  $\frac{B}{C}$  alone.*

We have already examined the influences on the drop-size in the case SLG of the density of the dropping liquid, and of its persistent and stubborn cohesions respectively. Increase in the former two tends to diminish the drop-size; increase in the last to increase it. Let us examine in like manner the influence of the similar properties of the medium.

1. *The density of the medium.*—Increase in the density of the medium is equivalent to diminution in the density of the dropping liquid, and must therefore be followed by a tendency to increase in the drop-size.

2. *Stubborn cohesion of medium.*—The resistance to displacement, or stubborn cohesion of the medium, tends to keep back the drop in its place, and makes it necessary for a larger quantity of the dropping liquid to accumulate; that is, it increases the drop-size.

3. *Retentive cohesion of medium.*—The same force of persistent or retentive cohesion which causes a drop of a liquid to take the spherical form, would also cause the liquid to give or tend to give a spherical form to an irregularly-shaped volume of a solid, liquid, gas, or vacuum in it. Thus gas-bubbles in liquids have an approximately spherical form, not by reason of the cohesion of the parts of the gas, but by the persistent cohesion of the liquid medium which moulds the gas into that form by which the cohesion of the liquid is most gratified. Hence increase in the retentive or persistent cohesion of the medium tends to diminish the drop-size of the dropping liquid.

In all cases of SLL we may represent the direction of the influence of the determinants by the following scheme, in which the sign + denotes a tendency to increase, the sign — one to diminish the drop-size :—

SLL.	
<i>Dropping Liquid.</i>	
+	—
Stubborn cohesion.	Persistent cohesion.
	Density.
<i>Medium Liquid.</i>	
+	—
Stubborn cohesion.	Persistent cohesion.
Density.	



This scheme is verified by the experimental results obtained. Of all liquids water forms the largest drops in falling through air, because in it the stubborn cohesion prevails to the greatest degree over the joint action of persistent cohesion and weight. In water mercury forms drops greater than in all other liquids, because in water (as a medium) stubborn cohesion and weight prevail to the greatest degree over persistent cohesion.

The case SLL may be inverted if the drop-forming liquid be specifically lighter than the medium liquid. Thus every case of SLL which we have examined in which a liquid, A, drops downwards through a liquid, B, has a counter case in which the liquid B drops upwards\* through the liquid A.

In order to measure the size of such ascending drops, the stalagmometer (fig. 7) is modified in form. It is not found possible to cause the dropping liquid to adhere with sufficient completeness and uniformity to a solid sphere immersed in the denser medium, in the cases experimented on. The end of the siphon A was turned upwards, and served as the solid whence the liquid dropped, without the interposition of a sphere or other solid. The measuring-tube D was removed from the neck of the cup C, a stopper being inserted in its place. The cup C was filled with water, and the measuring-tube D, being also filled with water, was inverted into it and supported by the holder H. The modified stalagmometer is seen in Plate V. fig. 10. Care was taken that the end of the siphon A should always be at the same depth beneath the surface of the water in C.

The drop-sizes of the liquids of Table XVI. were first examined by this stalagmometer.

The following Table XVII. shows the number of drops of the various liquids, dropping through water, required to fill the measuring-tube up to the given mark. The measuring-tube employed was different from that used in forming Table XVI. On this account, and because the delivering solid was quite different in shape, and *gt* only 2'', no immediate comparison can be made between Tables XVII. and XVI. In Table XVII. correction is made for meniscus.

TABLE XVII.

*gt* = 2''.

T = 24°·2 C.

T.	BT <sub>2</sub> .	BT.	B <sub>2</sub> T.	B.
287	252	229	205	103
287	252	231	205	104
287	251	230	207	104
287	251·7	230	205·7	103·7

We gather from this Table a law quite similar to that deduced from the measurement of the size of the downwards moving drops of water through these same liquids. It is as follows:—

*The drop-size of any mixture of two liquids, A and B, dropping up-*

\* See Part I. Introduction.

wards through a third liquid C, is intermediate between the drop-size of A through C and that of B through C; and the greater the proportion of  $\frac{A}{B}$  there is in the mixture, the more nearly does the drop-size of the mixture approach to the drop-size of  $\frac{A}{B}$  alone.

It is remarkable that supplementary drops are found in the cases just considered, just as in the case of water dropping through the same liquids. But the supplementary drops of benzol and turpental through water bear a much smaller ratio to the main drops than do those of water through benzol and turpental to their main drops. Judging only from the equality in their rate of ascent through the measuring-tube, all these supplementary drops are very exactly of the same size. The supplementary drops were not further examined, but were always collected and measured with the main drops.

Viewed as a means of quantitative chemical analysis, the measurement of the drop-sizes of liquids which drop up through water is yet more sensitive than that of the drop-sizes of water falling downwards through the liquids. Thus, from Table XVII., the least proportional difference of drop-number, caused by an alteration in the proportion of the liquids, is between T and BT<sub>2</sub>, where a diminution of 33·33 per cent. in the turpental and an addition of 33·33 per cent. of benzol causes a difference of 35·3 in the drop-number.

Liquid.....	T.	BT <sub>2</sub> .	BT.	B <sub>2</sub> T.	B.
Percentage.. { B=	0	33·33	50	66·66	100
{ T=	100	66·66	50	33·33	0
Difference of { B	33·33	16·66	16·66	33·33	
percentage.. { T	33·33	16·66	16·66	33·33	
Difference of { drop-number }	35·3	21·7	24·3	102·0	

Or this stalagmometer shows the composition of the liquid to within 1 per cent. Further, if the mixture contain less than one-third of benzol, we could determine the proportion, on an average, to within 0·33 per cent.

It may be noticed with regard to SLL that the value of *gt* is of much less influence upon the drop-size than in the case SLG. It is generally sufficient in the former case that the *average* value of *gt* should be constant. This is especially the case where the drops are formed from a tube (as the end of a siphon), and not from a convex solid. The reason is obviously that in the former case the thickness of the residual film, upon which we have found the size to depend, is at all rates indefinitely great, while in the latter case it depends upon the rate of supply.

In order to compare the drop-size of A through B with that of B through A under quite similar conditions, the siphon A of fig. 10 was inverted and applied to the cup stalagmometer of fig. 7. The arrangement of the end is seen in fig. 11. In using this form of stalagmometer, the end of the delivery-siphon must be at first wiped dry, so that the water may not

creep back along its outside, and so give rise to an irregular drop-base. Water was made to drop through A, fig. 11, at the same rate,  $gt=2''$ , and through the same liquids as before, namely T,  $BT_2$ , BT,  $B_2T$ , B. The same measuring-tube was used as in fig. 10, or Table XVII., and it was filled to the same point. Correction was made for meniscus.

TABLE XVIII.

 $gt=2''$ . $T=24^{\circ}5\text{ C.}$ 

	T.	$BT_2$ .	BT.	$B_2T$ .	B.
Number of drops. . . .	256	218	178	162	87
	256	220	177	164	86
	256	..	..	..	86
	..	..	..	..	86
	<u>256</u>	<u>219</u>	<u>177.5</u>	<u>163</u>	<u>86.2</u>

We may now compare Tables XVII. and XVIII., since the conditions of the experiments whence they are got are identical. The drop-sizes are inversely as the drop-numbers. Let us use the symbol  $X_y$  to denote the drop-size of the liquid X through medium Y, &c. Comparing, first, the size of a drop of X through medium Y with the size of a drop of Y through medium X, or finding the values of  $\frac{X_y}{Y_x}$ , we have (putting W for water)

TABLE XIX.

$$\begin{aligned}\frac{W_B}{B_W} &= \frac{103.7}{86.2} = 1.203. \\ \frac{W_{B_2T}}{B_2T_W} &= \frac{205.7}{163} = 1.262. \\ \frac{W_{BT}}{BT_W} &= \frac{230}{177.5} = 1.296. \\ \frac{W_{BT_2}}{BT_2W} &= \frac{251.7}{219} = 1.149. \\ \frac{W_T}{T_W} &= \frac{287}{256} = 1.121.\end{aligned}$$

Hence in none of these cases is the drop-size of one liquid through another equal to the drop-size of the second through the first. We get the general law, that—

*If the liquid X has a larger drop-size than the liquid Y in the liquid Z, then the liquid Z has a larger drop-size in X than it has in Y. Further,—*

*If a liquid X has a larger drop-size than a liquid Y in air, then the drop-size of X through Y is greater than the drop-size of Y through X. Again,—*

*If the drop-size of X be greater than the drop-size of Y, and the drop-size of Y be greater than the drop-size of Z in air, then the ratio between the drop-sizes of X in any mixture of Y and Z, and the drop-size of that*

*mixture of Y and Z through X, is greatest when the ratio between Y and Z is unity.*

From Tables XVII. and XVIII. we may gather an interesting fact, which illustrates other branches of physics. The drop-numbers of turpental and benzol through water being relatively 286 and 102, and the drop-numbers of water through benzol and turpental being relatively 256 and 86·2, we may construct the following Table, in which the theoretical numbers are compared with the experimental ones. The theoretical numbers are got as follows. *Ex.* :—

$$BT_2 = \frac{103\cdot7 + 2 \times 287}{3}.$$

$$BT = \frac{103\cdot7 + 287}{2}, \text{ \&c.}$$

	Theoretical.				
	T.	BT <sub>2</sub> .	BT.	B <sub>2</sub> T.	B.
Mixture of benzol and turpental through water..	287	225·9	195·3	164·8	103·7
	287	251·7	230	205·7	103·7
	Experimental.				
	T.	BT <sub>2</sub> .	BT.	B <sub>2</sub> T.	B.
Water through mixtures of benzol and turpental	256	199·4	171·1	142·8	86·2
	256	219	177·5	163	86·2

In all cases, then, the theoretical drop-number is less than the experimental one; or the theoretical drop-size is greater than the experimental one. Mixture impairs cohesion. Generally, when two solids are mixed, the melting-point of the two is lower than the mean of the melting-points of its components; sometimes lower than that of either. When two liquids are mixed, the boiling-point of the mixture (the initial boiling-point) is lower than that of either. The drop-size, which is also a function of the cohesion, we find here in no case to be less than the drop-size of either of the constituents, but in all cases to be less than the theoretical mean. Mixture impairs cohesion.

Further, comparing the drop-sizes of Table XVII. with one another, or all with B<sub>w</sub>, we get

TABLE XX.

$$\frac{B_w}{T_w} = \frac{287}{103\cdot7} = 2\cdot767.$$

$$\frac{B_w}{BT_2} = \frac{251\cdot7}{103\cdot7} = 2\cdot427.$$

$$\frac{B_w}{BT} = \frac{230}{103\cdot7} = 2\cdot227.$$

$$\frac{B_w}{B_2T_w} = \frac{205\cdot7}{103\cdot7} = 1\cdot983.$$

$$\frac{B_w}{B_w} = \frac{103\cdot7}{103\cdot7} = 1\cdot000.$$

In like manner, comparing the drop-sizes of Table XX. with one another, or with  $W_B$ , we have

TABLE XXI.

$$\begin{aligned}\frac{W_B}{W_T} &= \frac{256}{86 \cdot 2} = 2 \cdot 969. \\ \frac{W_B}{W_{BT_2}} &= \frac{219}{86 \cdot 2} = 2 \cdot 541. \\ \frac{W_B}{W_{BT}} &= \frac{177 \cdot 5}{86 \cdot 2} = 2 \cdot 059. \\ \frac{W_B}{W_{B_2T}} &= \frac{163}{86 \cdot 2} = 1 \cdot 890. \\ \frac{W_B}{W_B} &= \frac{86 \cdot 2}{86 \cdot 2} = 1 \cdot 000.\end{aligned}$$

Lastly, on comparing these figures with those of Table XX., we get the remarkable law, which it would be difficult to express in words, that

$$\frac{W_B \cdot T_W}{W_T \cdot B_W} = \frac{W_B \cdot BT_{2W}}{W_{BT_2} \cdot B_W} = \frac{W_B \cdot BT_W}{W_{BT} \cdot B_W} = \frac{W_B \cdot B_2T_W}{W_{B_2T} \cdot B_W} = 1 \text{ nearly.}$$

The main results with regard to drops may be collected into the following laws:—

## SLG.

*Law 1.*—The drop-size depends upon the rate of dropping. Generally, the quicker the succession of the drops, the greater is the drop; the slower the rate, the more strictly is this the case. This law depends upon the difference, at different rates, of the thickness of the film from which the drop falls.

*Law 2.*—The drop-size depends upon the nature and quantity of the solid which the dropping liquid holds in solution. If the liquid stands in no chemical relation to the solid, in general the drop-size diminishes as the quantity of solid contained in the liquid increases. The cause of this seems to be that the stubborn cohesion of the liquid is diminished by the solid in solution. Where one or more combinations between the liquid and solid are possible, the drop-size depends upon indeterminate data.

*Law 3.*—The drop-size depends upon the chemical nature of the dropping liquid, and little or nothing upon its density. Of all liquids examined, water has the greatest, and acetic acid the least drop-size.

*Law 4.*—The drop-size depends upon the geometric relation between the solid and the liquid. If the solid be spherical, the largest drops fall from the largest spheres. Absolute difference in radii takes a greater effect upon drops formed from smaller than upon those formed from larger spheres. Of circular horizontal planes, within certain limits, the size of the drop varies directly with the size of the plane.

*Law 5.*—The drop-size depends upon the chemical nature of the solid from which the drop falls, and little or nothing upon its density. Of all

the solids examined, antimony delivers the smallest, and tin the largest drops.

*Law 6.*—The drop-size depends upon temperature; generally, the higher the temperature the smaller the drop. With water, the effect of a change of temperature of  $20^{\circ}$  C. about  $30^{\circ}$  C. is very small.

*Law 7.*—The nature or tension of the gaseous medium has little or no effect upon drop-size.

#### SLL.

*Law 8.*—The drop-size of a liquid which drops under like conditions through various media, does not depend wholly upon the density of the medium and consequent variation in the weight, in the medium, of the dropping liquid.

*Law 9.*—If there be two liquids, A and B, which drop under like conditions through air, and the drop-size of the one, A, be greater than the drop-size of the other, B, then if a third liquid, C, be made to drop through A and through B, the drop-size of C through A is greater than the drop-size of C through B.

*Law 10.*—If the drop-size of A through B be greater than the drop-size of A through C, then the drop-size of a fourth liquid, D, through B is also greater than the drop-size of D through C.

*Law 11.*—If a liquid, A, drop under like conditions in succession through two liquids, B and C, then its drop-size through any mixture of B and C is intermediate between its drop-size through B and its drop-size through C. *Corr.* And the greater the proportion of  $\frac{B}{C}$  in the mixture the more nearly does the drop-size of A through the mixture approach to the drop-size of A through  $\frac{B}{C}$  alone.

*Law 12.*—The drop-size of any mixture of two liquids, A and B, dropping through a third liquid, C, is intermediate between the drop-size of A through C and that of B through C; and the greater the proportion of  $\frac{A}{B}$  in the mixture, the more nearly does the drop-size of the mixture approach to the drop-size of  $\frac{A}{B}$  alone, whether the dropping liquid be heavier or lighter than the liquid medium.

*Law 13.*—If the liquid X has a larger drop-size than the liquid Y in the liquid Z, then the liquid Z has a larger drop-size in X than it has in Y.

*Law 14.*—If a liquid, X, has a larger drop-size than a liquid, Y, in air, then the drop-size of X through Y is larger than the drop-size of Y through X.

*Law 15.*—If the drop-size of X be greater than the drop-size of Y in air, and the drop-size of Y be greater than the drop-size of Z in air, then the ratio between the drop-sizes of X in any mixture of Y and Z, and the drop-size of that mixture of Y and Z through X, is greatest when the ratio between Y and Z is unity.